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Measurement of Tropospheric Carbonyl
Sulfide by Microwave Spectrometry



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(NASA-CR-169417) MEASUREMENT OF
TROPOSPHERIC CARBONYL SULFIDE BY MICROWAVE
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Although Microwave Rotational Spectrometry (MRS) has been used very little in routine analysis, it has been shown (Varma and Hrubesh, 1979) to be a viable method for analysis of polar gases. The particular advantages of this form of spectrometry are 1) The extreme specificity, 2) wide dynamic range and 3) linear response with variation in concentration.

The high specificity of MRS arises from the high resolution ($\nu/\Delta\nu \approx 500,000$) and the unique spectrum for each particular molecular structure. The high resolution arises from the small doppler broadening at these frequencies and from operation at low pressures (10-100 mtorr) to reduce pressure broadening. The spectrum of a particular molecule is determined by the three principal moments of inertia, the dipole moment direction within the molecule and selection rules for transitions, hence is unique for that molecule. For example, the strong line at 36488.812 MHz of OCS has a linewidth [full width at half maximum (FWHM)] of about .120 MHz at 100 mtorr and the nearest known microwave spectral line of another substance is about 1 MHz away. Similar conditions exist for SO_2 and other microwave absorbers, hence, the accurate determination of the frequency of maximum absorption uniquely determines the identity of the absorber.

The wide dynamic range and linear response are inherent in this form of spectrometry. Varma and Hrubesh (1979) derive the expression:

$$p_p = K S_p \frac{\Delta\nu(\lambda/\lambda_0)}{T^{3/2}} \quad (1)$$

where p_p is the partial pressure of a component in a mixture, K is a proportionality constant, S_p is the peak absorption signal, $\Delta\nu$ is the

half width at half height of the absorption line, and λ and λ_g are the wavelength and guide wavelength respectively. Since K is actually constant, a measurement of S_p and $\Delta\nu$ and the total pressure give the concentration of that component over many orders of magnitude.

The integrated absorption coefficient, α_{int} , can be expressed (Varma and Hrubesh, 1979) as

$$\alpha_{int} = \pi U \nu_0^2 \cdot x \cdot p \quad (2)$$

where U is a constant for a given transition and temperature, ν_0 is the center frequency of the absorption line, x is the mole fraction of the molecular species, and p is the total gas pressure. The determination of the integrated intensity requires the measurement of the signal vs frequency at many frequencies over the line profile. This can be done easily under computer control, and allows the operator to observe the line shape to confirm the existence and identity of the line. A further advantage is a very large increase in signal to noise ratio after integration over the line profile. This method is not dependent upon an ideal Lorentzian line shape. The instrument used in this study consists of a much modified Hewlett-Packard model 8400 B microwave rotational spectrometer which was interfaced to a Commodore Microcomputer shortly before this work started. Programs written during this study step the microwave source over the spectral line, acquire the signal and allow for many such sweeps to be averaged. The result can be plotted on an x-y plotter or printed. Such a plot is shown in Fig. 1 for a 1% sample of OCS in N_2 . Both the signal and the "running sum" of the signal values are plotted. The resulting sum is the integrated intensity of

the line. A region can be noted toward the left of the line center where both the signal and sum are negative. This is an incompletely resolved stark lobe. Because of this, subsequent data runs went only from the line center upwards. This method was used for calibration, as shown in figures 2 and 3. The integrated intensity can be seen, in Fig. 3, to be very linear with partial pressure of the absorber. The intercept at zero pressure approaches zero signal as the mixing ratio is reduced. Figure 4 is the integrated signal from a 9.7 ppmv test sample at a cell pressure of 57.4 milli torr demonstrating the sensitivity. This requires about 2 hours of averaging time, indicating that a substantial preconcentration step was required.

Preconcentration methods which have been used with MRS include cryogenic methods and adsorption concentration. In the first methods, all condensible components are frozen out with LN_2 and the air then pumped off. The remaining sample is allowed to return to room temperature in the same volume. Pressure measurements before and after this step give the percentage of condensibles. The MRS signal resulting from an aliquot of this sample then gives the partial pressure or mole fraction of the species in question, and the concentration in the original sample is found from the pressure ratio previously recorded. The adsorption concentration method consists of passing a large sample of air through a small plug of adsorptive material at relatively low temperature. The plug is then recovered and the adsorbed gases driven off with heat.

After examining and trying many adsorptive materials and various techniques, the following method evolved. A flowing air sample is passed first through a P_2O_5 drying tube, (since the large amount of

moisture collected will mask the OCS quantity in the cell. (the low measurement pressure required) then through a glass U tube containing silica gel. This U tube was chilled at 0°C to enhance the adsorption efficiency. Tests, using the dynamic dilution system in Fig. 5 indicated no loss of OCS to the P_2O_5 . After a time determined by the calibrated flow rate to pump 1000 liters of air through the sampler, it was valved off and taken to the laboratory. The U tube was then attached to a sample volume (of known volume) and dry, hot N_2 passed through it. A second U tube was maintained at liquid N_2 to trap the sample. After about 30 min., flow was stopped and the N_2 pumped away. The sample then was warmed to room temperature, and the pressure measured. From the barometric pressure, and the sample volume pressure and known volumes, a concentration ratio was determined.

Aliquots of the sample were then admitted to the microwave absorption cell and the integrated intensity measured. The results of one such measurement are shown in Fig. 6. From the amount of air passed through the U tube (5.82 torr liters) and the measured amount of dry condensate (.032 torr liters) a concentration ratio, for this sample, was determined (1.828×10^7). The microwave measurements, along with previously determined calibration factors, resulted in a mixing ratio in the dry condensate of 2.51×10^{-3} . This indicated that the original air sample mixing ratio was 1.37×10^{-10} . This value for this particular sample is considerably lower than previous measurements using other methods. This may be due to less than 100% adsorption efficiency in the silica gel, or to adsorption of OCS within the system (although it was passivated with hexamethyldisilazane). The previous tests with known trace mixtures would indicate, however, that the low value is real.

This sample was collected at the U.W. Balloon Launch Facility far from possible anthropogenic sources of carbonyl sulfide.

The results of this study do indicate that with proper sampling procedures, the sensitivity is available for the measurement of OCS ambient levels. Since the sensitivity is depending upon v_0^2 (among other factors) higher frequency operation would allow much smaller samples to be collected, and would eliminate some of the sampling problems. To completely eliminate these problems, some sort of "in-situ" method would be preferred.

0CS-1%

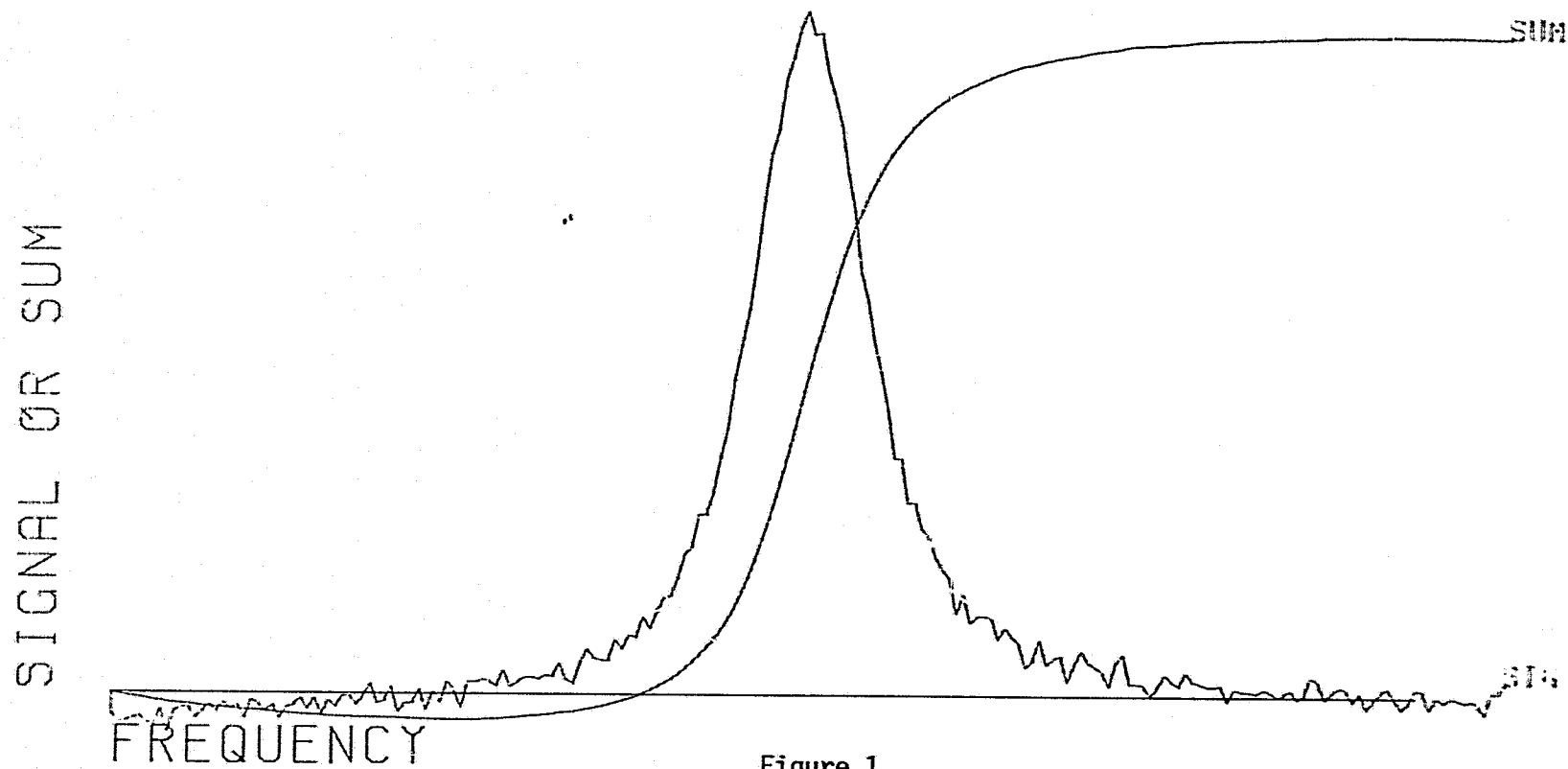
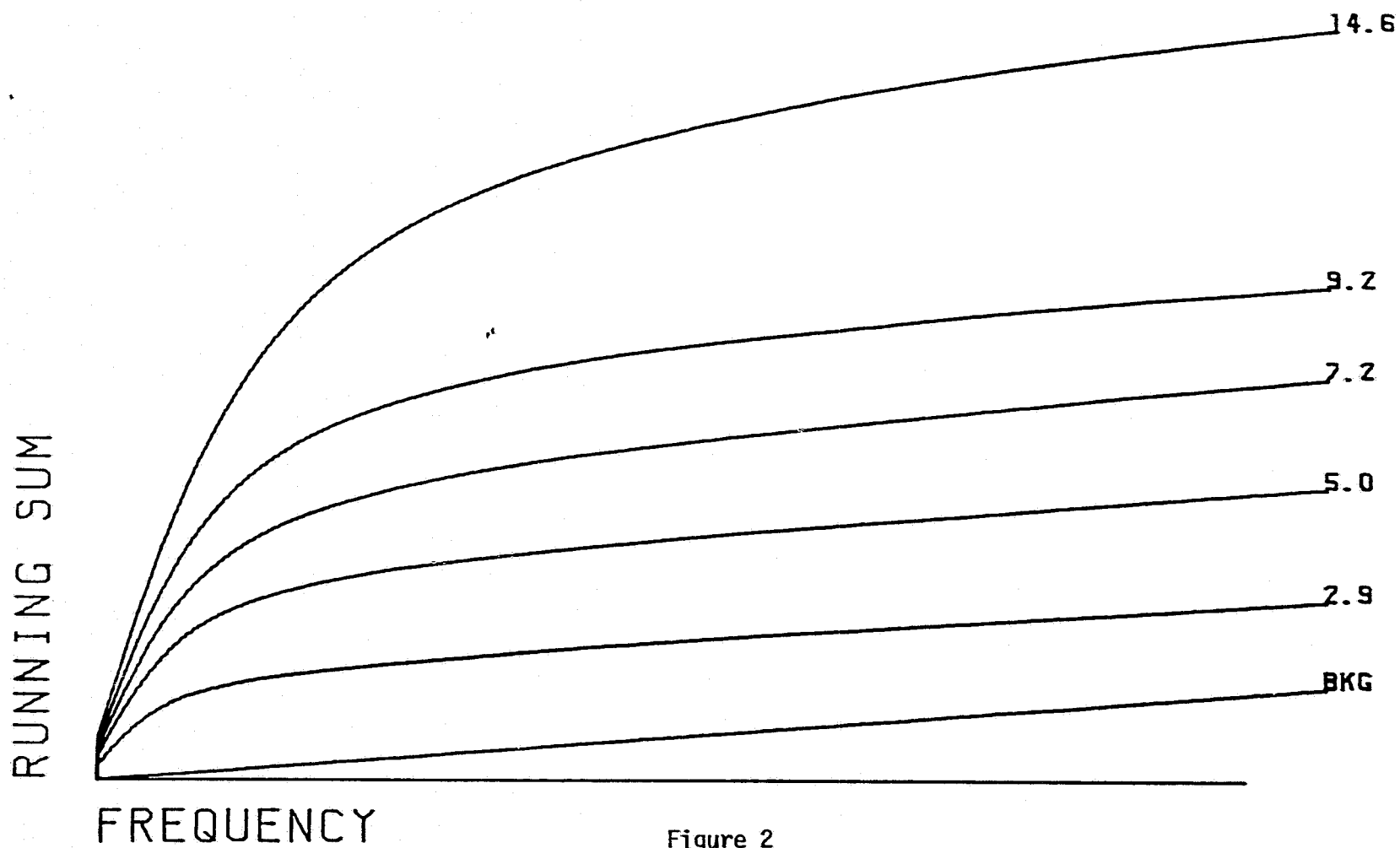


Figure 1

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OCS CALIBRATION



ORIGINAL RECORD
OF POOR QUALITY

Figure 2

OCS-100%

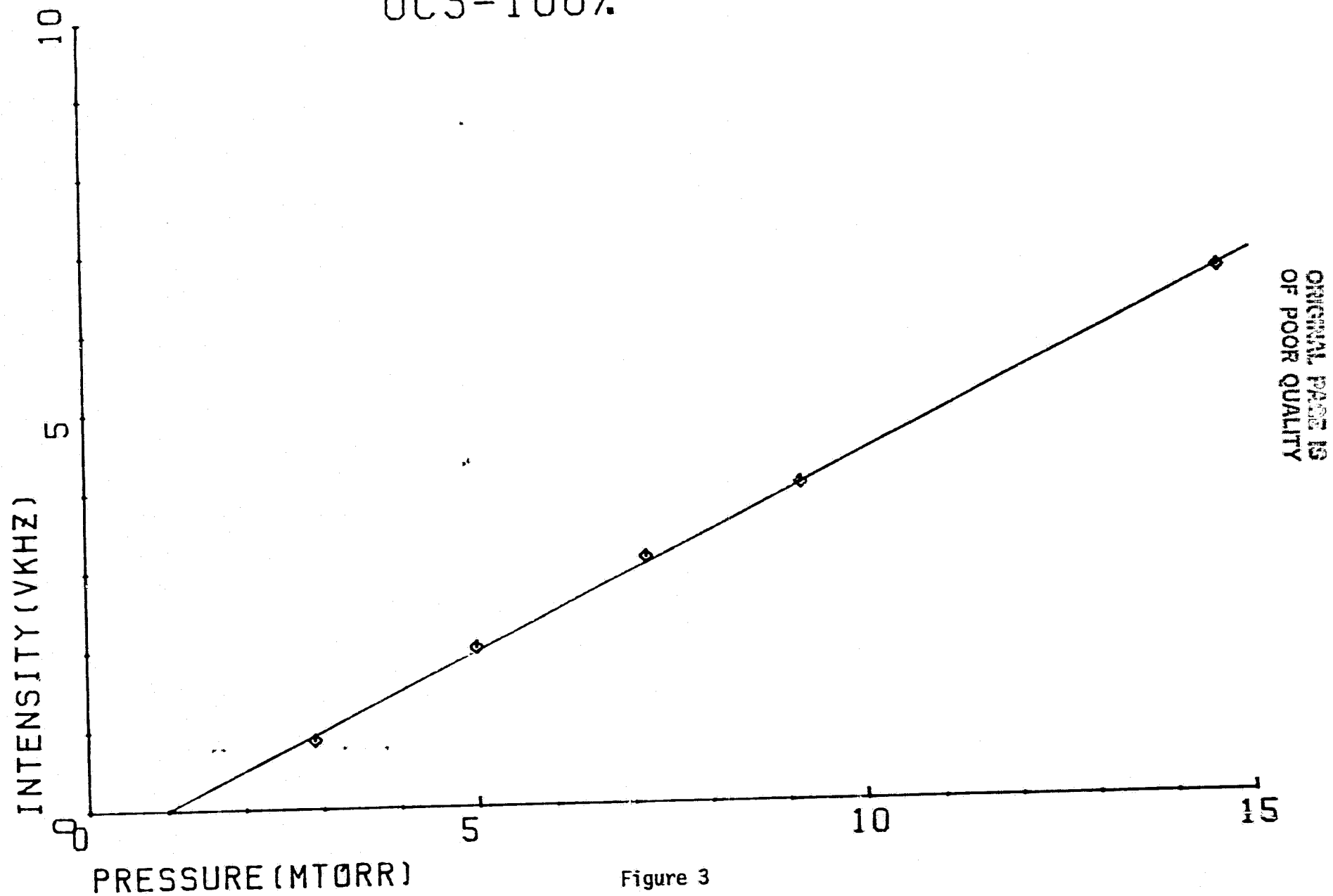


Figure 3

0CS-9.7PPM

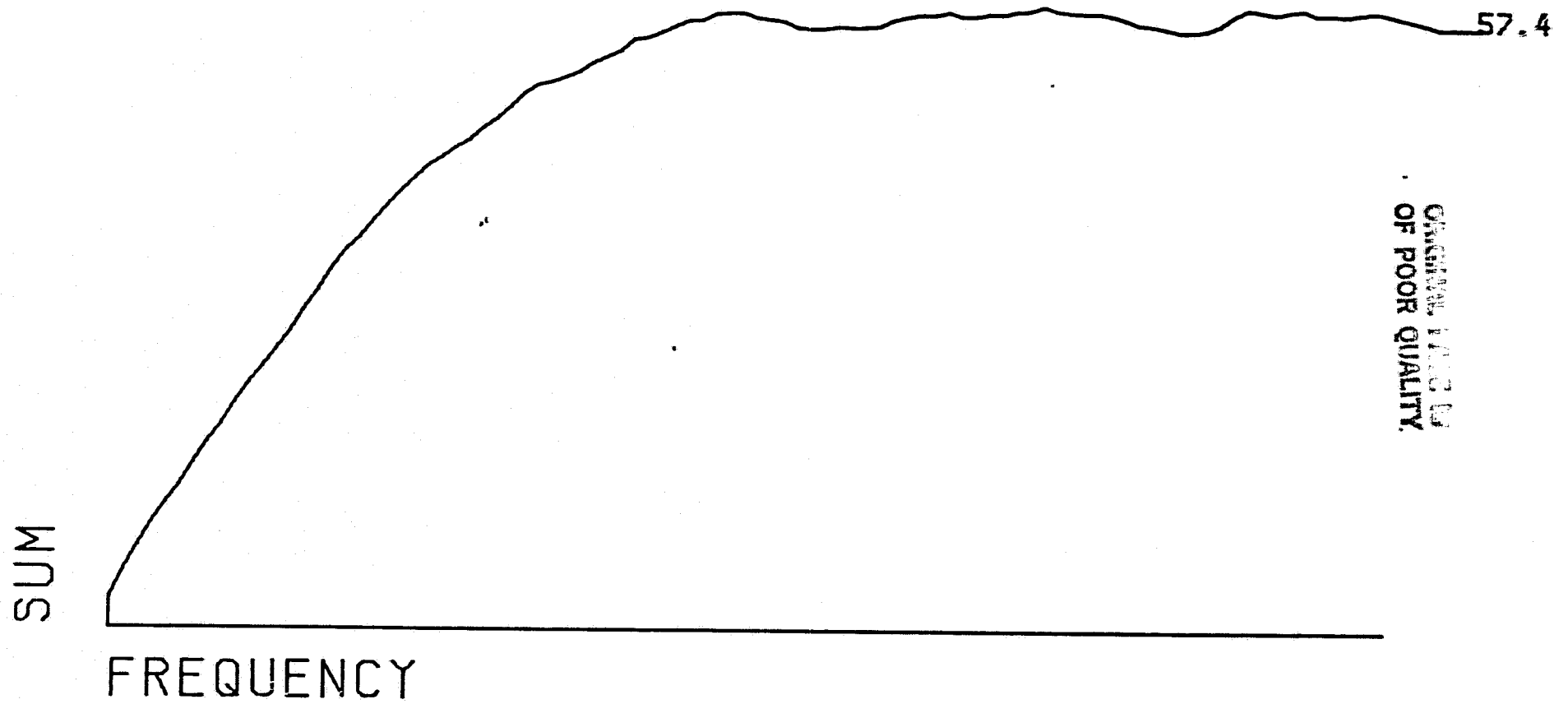
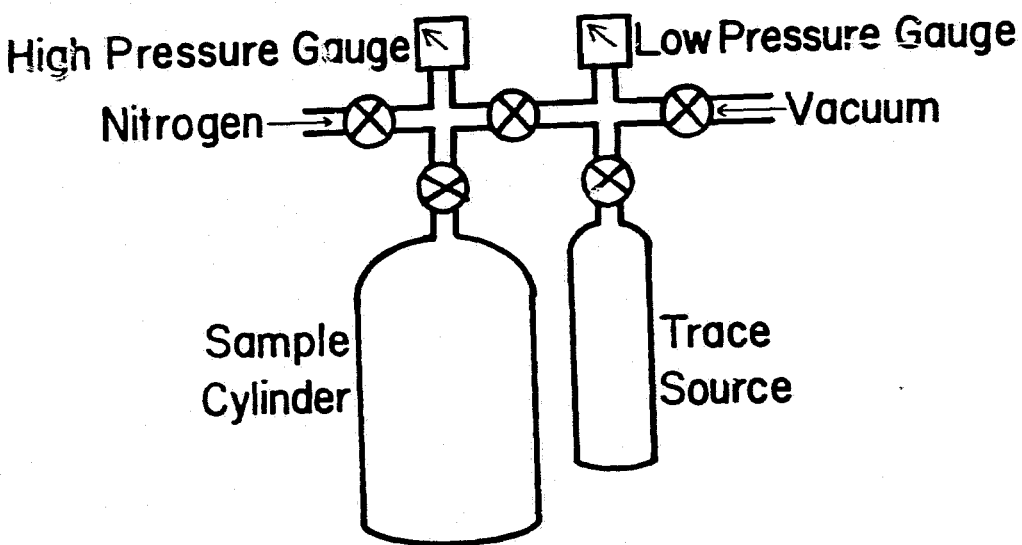


Figure 4

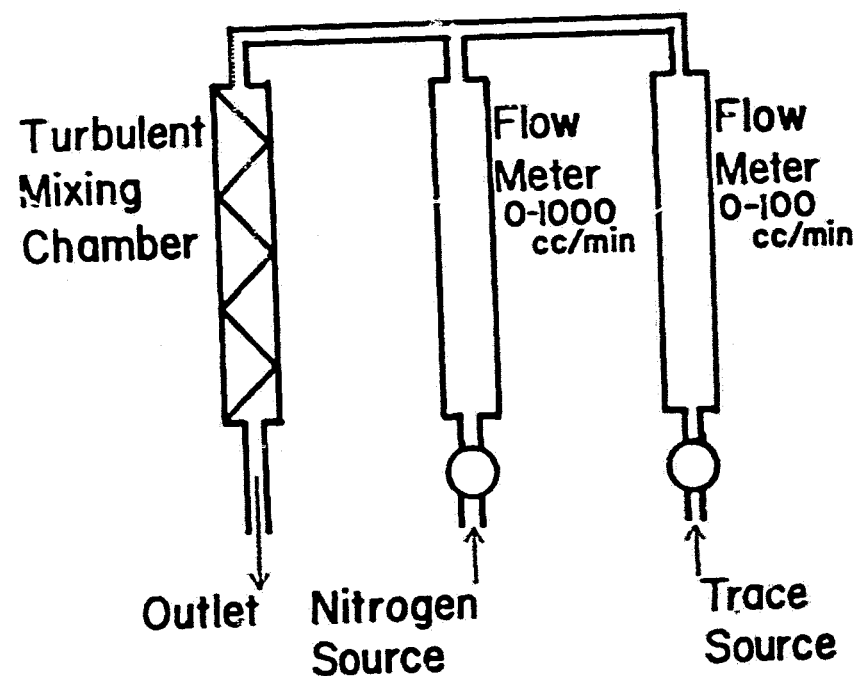
Static Dilution System



PROCEDURE:

- 1) Deliver 50 millitorr of trace gas to sample cylinder
- 2) Allow 24 hours time for possible uptake on cylinder walls
- 3) Backfill with 5,000 torr of nitrogen

Dynamic Dilution System



Dynamic range of system: 10ppm – 10ppb

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Figure 5

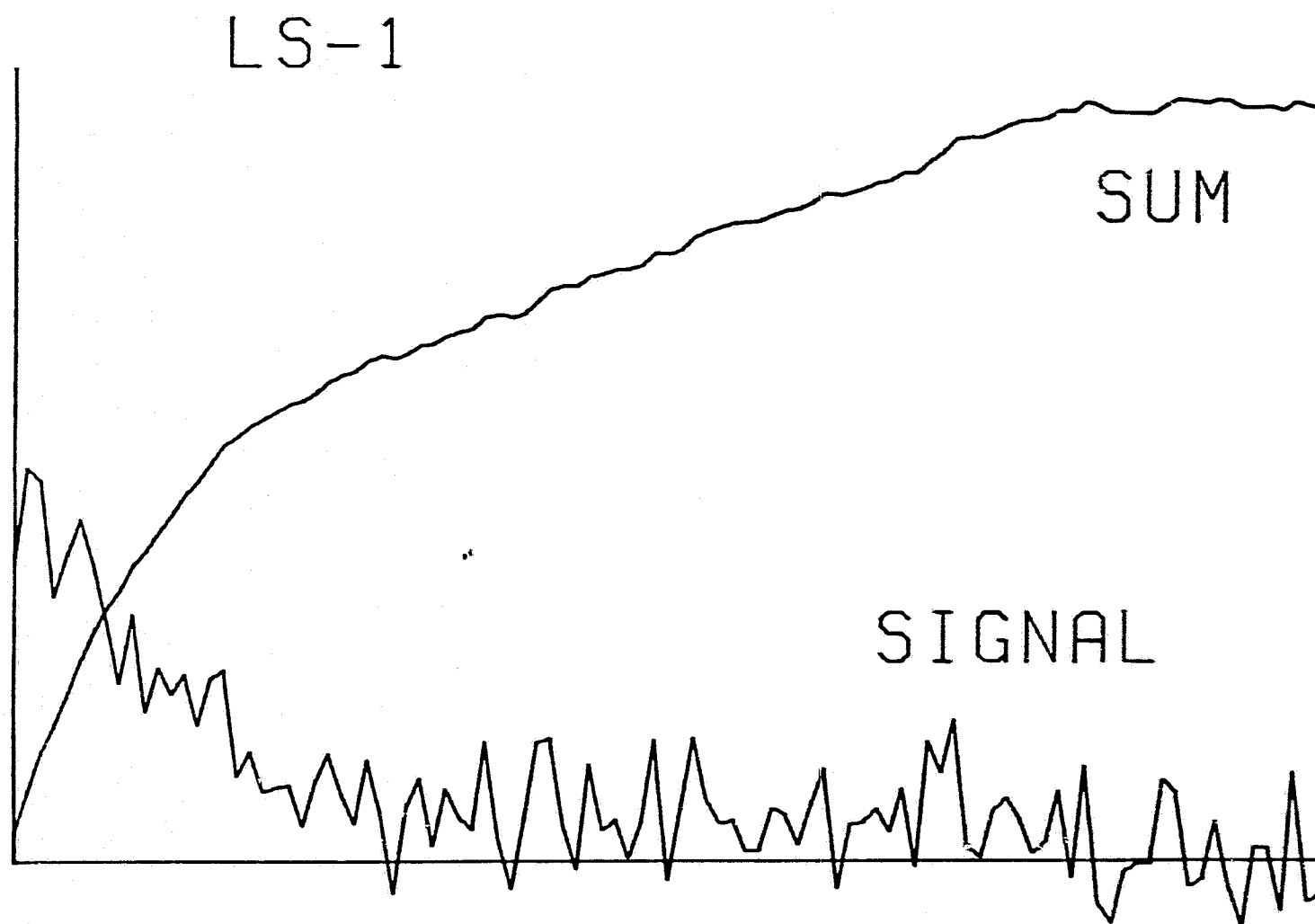


Figure 6

Figure Captions

Figure 1. The microwave signal (SIG) and the running sum vs frequency for carbonyl sulfide at a 1% mixing ratio. The negative going signal and sum at a lower frequency than the linecenter is due to an incompletely resolved stark lobe.

Figure 2. Running sums of the microwave signal for the upper half of the carbonyl sulfide absorption line. The numbers to the right represent the cell pressure in milli torr. BKG is the background signal.

Figure 3. The calibration curve resulting from data in Fig. 2. With reduced mixing ratios, the zero pressure intercept approaches the origin, but the slope remains constant at .488 V Khz/intorr.

Figure 4. The resulting integrated intensity for a 9.7 ppm sample of carbonyl sulfide in nitrogen.

Figure 5. Dilution systems used to produce standard gas mixtures.

Figure 6. The signal and sum for the dry condensable fraction of a 1000 μ sample collected west of Laramie, WY.